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Full length article

Theoretical study of elastic, mechanical and thermodynamic properties of MgRh intermetallic compound

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Abstract

In the last years, Magnesium alloys are known to be of great technological importance and high scientific interest. In this work, density functional theory plane-wave pseudo potential method, with local density approximation (LDA) and generalized gradient approximation (GGA) are used to perform first-principles quantum mechanics calculations in order to investigate the structural, elastic and mechanical properties of the intermetallic compound MgRh with a CsCl-type structure. Comparison of the calculated equilibrium lattice constant and experimental data shows good agreement. The elastic constants were determined from a linear fit of the calculated stress−strain function according to Hooke's law. From the elastic constants, the bulk modulus B, shear modulus G, Young's modulus E, Poisson's ratio σ, anisotropy factor A and the ratio B/G for MgRh compound are obtained. The sound velocities and Debye temperature are also predicted from elastic constants. Finally, the linear response method has been used to calculate the thermodynamic properties. The temperature dependence of the enthalpy H, free energy F, entropy S, and heat capacity at constant volume C_v of MgRh crystal in a quasi-harmonic approximation have been obtained from phonon density of states and discussed for the first report. This is the first quantitative theoretical prediction of these properties.

Keywords: Intermetallics; Elastic properties; Mechanical properties; Thermodynamic properties; Computer simulations

1. Introduction

Magnesium (Mg), with its abundance in the Earth is becoming an important engineering material. The last years, significant progress was made on the science, technology and application of magnesium and its alloys. Research on Mg based alloys is of particular interest due to its low density (~1.74 g/cm^3) and high specific strength and stiffness than many other engineering materials, including aluminum, steel and polymer-based composites. Magnesium also possess many other attractive properties, such as a high damping capacity, electromagnetic shielding, thermal conductivity, good machinability and high recycling potential [1]. Magnesium alloys are among the lightest structural materials known and are used in a variety of applications, particularly in automobile industry and aerospace manufacturing [2]. The above-mentioned features motivated us to study these alloys.

Magnesium forms a wide range of ordered intermetallic compounds with the 4d transition metals (TM), for example the compound MgRh was prepared by heating the elements in stoichiometric proportion and the reaction was carried out in fused quartz tube at 1000 °C. The crystal structure of MgRh compound was determined by X-ray powder diffraction, and it crystallizes in B2 type structure [3]. To the best of our knowledge, the intermetallic compound MgRh has not been

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studied neither experimentally nor theoretically. Thus, in this work we have carried out a theoretical investigation on the structural, elastic, mechanical and thermodynamic properties of MgRh alloy, in order to provide a sounder basis for further experimental and theoretical studies. Ab initio methods offer one of the most powerful tools carrying out theoretical investigation of an important number of physical and chemical properties of materials with a great accuracy. The rest of this paper is organized as follows: the computational method is described in Section 2, the numerical results and discussions are given in Section 3, and finally a conclusion is presented in Section 4.

2. Computational method

Our first-principles quantum mechanics calculations are performed with the plane-wave pseudo-potential (PW-PP) total energy method implemented with the CASTEP (Cambridge Serial Total Energy Package) simulation program [4]. This is based on the density functional theory (DFT) [5,6] which is, in principle, an exact theory of the ground state. We have used two approximations. First, the local density approximation (LDA) developed by Ceperley and Adler and parameterized by Perdew and Zunger [7,8], as well as the generalized gradient approximation (GGA), with the new functional of Perdew–Burke–Ernzerhof (PBE), known as PBEsol [9], are made for electronic exchange-correlation potential energy. Second, Coulomb potential energy caused by electron–ion interaction is described using the Vanderbilt-type ultrasoft scheme [10], in which the orbitals of Mg ($2p^6 3s^2$), Rh ($4d^8 5s^1$), are treated as valence electrons. The cut-off energy for the plane-wave expansion was chosen at 340 eV and the Brillouin zone sampling was carried out using the $8 \times 8 \times 8$ set of Monkhorst–Pack mesh [11].

The structural parameter (a) of MgRh was determined using the Broyden–Fletcher–Goldfarb–Shenno (BFGS) minimization technique [12]. This method usually provides the fast way of finding the lowest energy structure.

In the structural optimization process, the energy change, maximum force, maximum stress and maximum displacement are set as 1.0×10^{-5} eV/atom, 0.03 eV/Å, 0.05 GPa, and 0.001 Å, respectively.

The elastic constants were determined from first-principles calculations by applying a given homogeneous strain (deformation) with a finite value and calculating the resulting stress according to Hook's law [13]. The total energy is converged to 2.0×10^{-6} eV/atom in the self-consistent calculation.

The thermodynamic properties of a crystal in a quasi-harmonic approximation have been predicted using phonon calculations with the linear response method.

3. Results and discussion

3.1. Structural properties

The atomic structure of MgRh intermetallic compound is known to crystallize in a cubic lattice of CsCl-type structure (B2) with the space group Pm-3m (221) and the equilibrium lattice parameter has a value of (3.099 ± 0.002) Å [3]. The unit cell structural model of the MgRh compound is built according to the experimental data [3], as shown in Fig. 1. The crystal structure was optimized at first. The obtained results of calculated lattice parameter a of MgRh intermetallic compound using the (PW-PP) method within both the LDA and the GGA-PBEsol approximations are 3.053 Å and 3.101 Å respectively. One can see from the present results that the calculated lattice constant a is 1.4% smaller than the experimental value using LDA and it is only 0.06% higher than the experimental value using GGA-PBEsol. Our calculated equilibrium lattice parameter agrees very well with the experimental data, above all in GGA approximation.

3.2. Elastic and mechanical properties

Elastic constants are very important material parameters. Evident and direct application of elastic constants is in the evaluation of elastic strains or energies in materials under stresses of various origins: external, internal and thermal [14]. The elastic constants can also provide information on the stability, stiffness, brittleness, ductility, and anisotropy of a material and propagation of elastic waves and normal mode oscillations. Moreover, knowledge of the values of elastic constants is crucial for a sound understanding of the mechanical properties of the relevant material.

The elasticity of a cubic crystal is specified by the three independent elastic constants C_{11}, C_{12} and C_{44}. In this work, the calculated elastic constants of MgRh compound at zero pressure and temperature are presented in Table 1. For a cubic crystal, the obtained elastic constants meet the requirements of mechanical stability criteria: $C_{11} > 0$, $C_{44} > 0$, $C_{11} - C_{12} > 0$, $C_{11} + 2C_{12} > 0$ and $C_{11} > B > C_{12}$. From Table 1, one can see that the elastic constants of MgRh compound satisfy all of these conditions, suggesting that the structure of MgRh is mechanically stable. The elastic constants values calculated using the LDA approximation are slightly higher than those obtained with the GGA-PBEsol approximation. To the best of our knowledge, there are no experimental and other theoretical data in literature for the elastic constants (C_{ij}) of MgRh for comparison, so we consider the present results as prediction study which still awaits an experimental confirmation. The

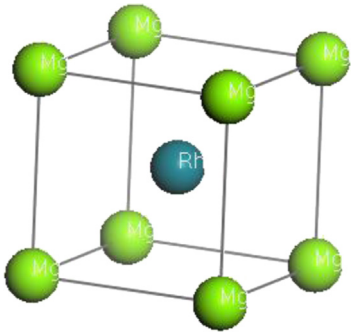

Fig. 1. Crystal structure of MgRh.

Table 1
Calculated values of the elastic constants C_{ij} (GPa), bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa), Poisson's ratio σ, anisotropy factor A and B/G of MgRh compound.

	C_{11}	C_{12}	C_{44}	B	G	E	σ	A	B/G
This work									
LDA	186.99	113.69	81.80	138.12	59.27	101.02	0.38	2.23	2.33
GGA	172.45	102.22	77.41	125.63	56.36	96.37	0.37	2.20	2.23
Exp.	–	–	–	–		–	–	–	–
Other	–	–	–	–		–	–	–	–

most important parameters for estimating mechanical properties of materials such as bulk modulus (B), shear modulus (G), Young's modulus (E) and Poisson's ratio (σ) are obtained from results of the calculated single-crystal elastic constants C_{ij} using the Voigt–Reuss–Hill (VRH) averaging scheme [15]. The Voigt–Reuss–Hill approximation gives the effective values of the bulk and shear moduli. For the cubic system, the Voigt bounds [16] of the bulk modulus B_V and shear modulus G_V are:

$$B_V = \frac{(C_{11} + 2C_{12})}{3} \tag{1}$$

and

$$G_V = \frac{(C_{11} - C_{12} + 3C_{44})}{5} \tag{2}$$

The Reuss bounds [17] of the bulk and shear moduli are:

$$B_R = B_V \tag{3}$$

and

$$G_R = \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})} \tag{4}$$

Finally, the bulk modulus B and shear modulus G, based on Hill approximation [15] are arithmetic average of Voigt and Reuss elastic moduli. They are expressed as following:

$$B = \frac{1}{2}(B_V + B_R) \tag{5}$$

and

$$G = \frac{1}{2}(G_V + G_R) \tag{6}$$

Young's modulus (E) and Poisson's ratio (σ) can be calculated by using Hill's elastic moduli (B) and (G), which are given as:

$$E = \frac{9BG}{3B + G} \tag{7}$$

$$\sigma = \frac{3B - 2G}{2(3B + G)} \tag{8}$$

The calculated results for these moduli and Poisson's ratio for the MgRh compound are listed in Table 1. The bulk modulus is usually assumed to be a measure of resistance to volume change by applied pressure. From Table 1, it can be seen that the value of the bulk modulus of MgRh compound is larger, indicating that it has a strong resistance to volume change by applied pressure. The two constants E and G, are all that are needed to fully characterize the stiffness of an isotropic material. The present calculated results of these moduli demonstrate that the MgRh compound is stiff. The Poisson's ratio (σ) defined as the ratio of transverse strain to the longitudinal strain is used to reflect the stability of the material against shear and provides information about the nature of the bonding forces. It takes the value: $-1 < \sigma < ½$. No real material is known to have a negative value of σ. So this inequality can be replaced with $0 < \sigma < ½$. The low value of Poisson's ratio indicates a large compression of volume and when $\sigma = 0.5$ no volume change occurs. Bigger the Poisson's ratios better the plasticity. The present calculated result of the Poisson's ratio shows that the MgRh intermetallic compound is of good plasticity. The $\sigma = 0.25$ and $\sigma = 0.5$ are the lower limit and upper limit for central forces in solids, respectively. The obtained value of Poisson's ratio (σ) of MgRh is larger than the lower limit value ($\sigma = 0.25$), which indicates that the interatomic forces of MgRh are central forces.

The Zener anisotropy factor (A) is a measure of the degree of anisotropy in solid [18]. It takes the value of 1 for an isotropic material. It provides a measure of the degree of elastic anisotropy, when the A values are smaller or greater than unity. The Zener anisotropy factor (A) Of MgRh compound is calculated by the following equation:

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \tag{9}$$

As shown in Table 1, that the calculated Zener anisotropy factor A is larger than 1 for both approximations LDA and GGA, which indicates that, the MgRh compound is elastically anisotropic material.

The ratio B/G is a simple relationship related to brittle or ductile behavior of materials. It has been proposed by Pugh [19]. A high B/G ratio is associated with ductility, whereas a low value corresponds to the brittleness. The critical value separating ductile and brittle material is 1.75. The calculated results are listed in Table 1. In this work, the obtained results of both approximations LDA and GGA indicate that MgRh compound can be classified as ductile material at zero pressure. Another parameter indicating the brittleness or ductility of the material is the Cauchy relation defined as: $C_P = C_{12} - C_{44}$. The material is expected to be ductile, if the value of this expression is positive, on the other hand, if its value is negative, the material is brittle [20]. At zero pressure, we found 31.89 GPa and 24.81 GPa for Cauchy pressure within both the LDA and the GGA approximations respectively. From these values and according to above criterion, the studied compound is ductile. Thus, the ductile nature of MgRh compound can be related to a metallic character in its bonds.

3.3. Thermodynamic properties

The Debye temperature (Θ_D) of a material is a suitable parameter to describe phenomena of solid-state physics which

Table 2
The calculated density ρ, the longitudinal, transverse and average sound velocities (v_l, v_t and v_m) calculated from elastic moduli, and the calculated Debye temperatures Θ_D for MgRh compound.

	ρ (g cm^{-3})	v_l (m s^{-1})	v_t (m s^{-1})	v_m (m s^{-1})	Θ_D (K)
This work					
LDA	7.4250	5407.90	2825.33	3161.04	389
GGA	7.0835	5323.95	2820.74	3152.76	382
Exp.	–	–	–	–	–
Other	–	–	–	–	–

are associated with lattice vibrations. The Debye temperature corresponds in the Debye theory to a maximum phonon frequency. In addition, it reflects the structural stability, the strength of bonds and it is closely related to many physical properties such as specific heat and melting temperature. The Debye temperature basically depends on the elastic constants. At low temperature the Debye temperature calculated from elastic constants is the same as that determined from specific heat measurements. One of the standard methods to calculate the Debye temperature (Θ_D) is from elastic data, since Θ_D may be estimated from the average sound velocity v_m by the following equation [21]:

$$\Theta_D = \frac{h}{k_B}\left(\frac{3n}{4\pi V_a}\right)^{\frac{1}{3}} v_m \tag{10}$$

where h is Plank's constant, k_B Boltzmann's constant, n is the number of atoms per formula unit and V_a the atomic volume. The average sound velocity in the polycrystalline material is given by the following equation [22]:

$$v_m = \left[\frac{1}{3}\left(\frac{1}{v_l^3}+\frac{2}{v_t^3}\right)\right]^{-\frac{1}{3}} \tag{11}$$

where v_l and v_t are the longitudinal and transverse sound velocities of an isotropic aggregate, obtained using the shear modulus G and the bulk modulus B from Navier's equation [23]:

$$v_l = \left(\frac{3B+4G}{3\rho}\right)^{1/2} \tag{12}$$

and

$$v_t = \left(\frac{G}{\rho}\right)^{1/2} \tag{13}$$

The calculated Debye temperature (Θ_D) and sound velocities (v_m, v_l, v_t) as well as the density (ρ) for MgRh compound in both approximations LDA and GGA are listed in Table 2. To the best of our knowledge, there are no experimental and other theoretical data for comparison, so we consider the present results as a prediction study for the first time, which still awaits an experimental confirmation.

In order to evaluate the temperature dependence of the enthalpy H, free energy F, entropy S, and heat capacity at constant volume C_v of a crystal in a quasi-harmonic approximation, we need to calculate the phonon density of states

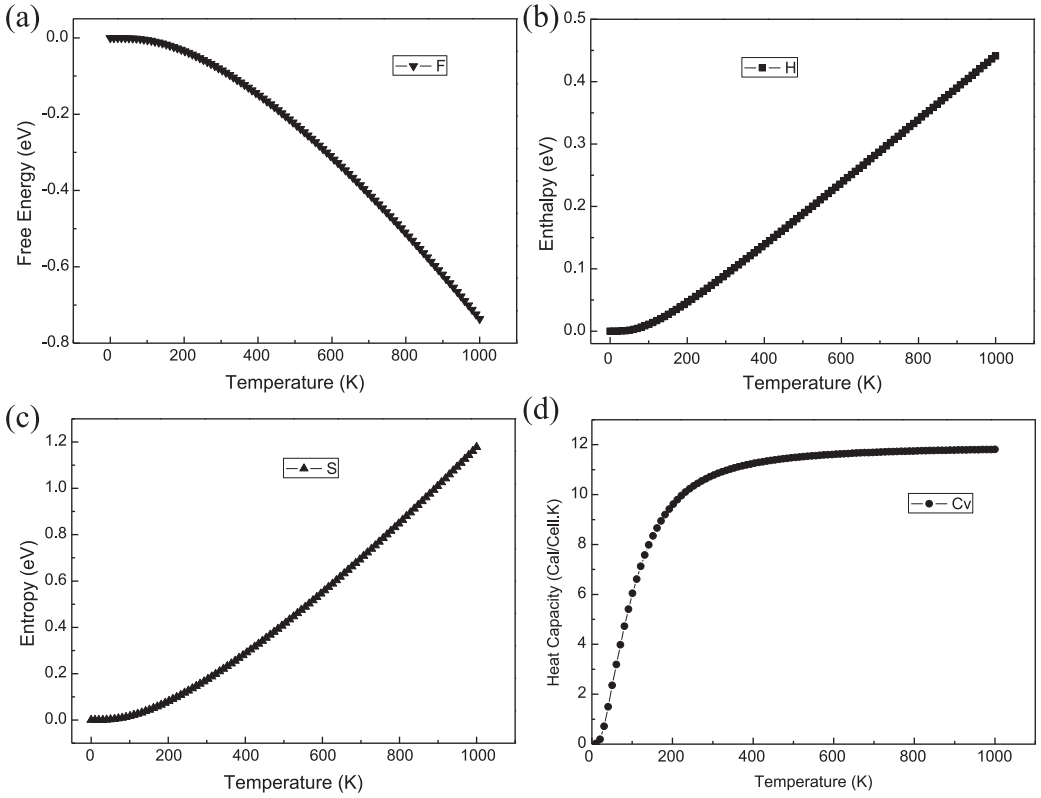

Fig. 2. (a). Temperature dependence of the free energy for MgRh. (b). Temperature dependence of the enthalpy for MgRh. (c). Temperature dependence of the entropy for MgRh. (d). Temperature dependence of the heat capacity at constant volume for MgRh.

(PDOS), which can obtained by performing phonon calculations. In this work, the phonon contribution to the free energy F, to the enthalpy H, to the entropy S and to the specific heat C_v at temperature for MgRh intermetallic compound, are shown in Fig. 2. The calculated value of zero point energy at 0 GPa is 0.0808 eV. From Fig. 2(a), we can see that the free energy decreases gradually with increasing temperature. In Fig. 2(b) and (c), as temperature increases, the calculated enthalpy H, and entropy S increase continually. At ambient temperature, the heat capacity C_v is 10.71 Cal/Cell K and it tend to the asymptotic limit (so called the Dulong−Petit limit) of $C_v = 11.80$ Cal/Cell K $= 3nNk_B$ at higher temperatures, as is shown in Fig. 2(d). The experimental thermodynamic data of MgRh cannot be found, therefore it is difficult to evaluate the magnitude of errors between theory and experiment. Our calculated results can be seen as a prediction study for future investigations.

4. Conclusions

In the present theoretical study, the structural, elastic, mechanical, and thermodynamic properties of MgRh intermetallic compound with a CsCl-type structure have been investigated by means of the DFT within LDA and GGA approximations. Our results for the optimized lattice parameter (a) are in good agreement with the available experimental data. The elastic constants C_{ij}, and related polycrystalline mechanical parameters such as bulk modulus B, shear modulus G, Young's modulus E and Poisson coefficient σ are calculated. The MgRh compound is mechanically stable according to the elastic stability criteria, while no experimental results of elastic moduli for comparison. The Zener factor A, the B/G ratio and Cauchy pressure ($C_{12}-C_{44}$) are also estimated. The calculated Zener factor indicates that MgRh compound is elastically anisotropic. The values of the ratio B/G and Cauchy pressure show a ductile manner for the MgRh compound. Finally, from the knowledge of the elastic constants and the average sound velocities and through the quasi-harmonic Debye model using the calculated PDOS the thermodynamic properties have been predicted successfully. The heat capacity at constant volume of MgRh increases sharply with temperature at low temperature and it tends to Dulong−Petit limit at high temperature.

Acknowledgments

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